



Optimizing the electrochemical performance of aqueous symmetric supercapacitors based on an activated carbon xerogel



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H I G H L I G H T S

- Highly micro-mesoporous carbon xerogels were used as electrodes in aqueous supercapacitors.
- The electrodes preparation procedure significantly affects their electrical and mechanical properties.
- The electrolyte pH and the chemical nature of carbon xerogel influence the energy storage.
- C values of $\sim 200 \text{ F g}^{-1}$ were achieved with H_2SO_4 electrolyte medium which producing higher charge storage.

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A highly porous carbon xerogel was synthesized by means of physical activation. The activated carbon xerogel, which displayed a well-developed porous texture (micro- and meso-porosity), was employed as electrode material in different supercapacitors. In assessing the performance of the supercapacitors, special attention was paid to their dimensions and the type of electrolyte used. Both the method of electrode manufacture (rolling and punching of 1 cm^2 pellets vs. casting by means of a film applicator to produce 4 cm^2 electrodes) and the type of supercapacitor (Swagelok (R) system vs. cell with graphite plate current collectors) were evaluated. The results reveal that the cells with larger electrodes were able to store higher amounts of energy. In addition to the cells, the electrochemical characteristics in aqueous electrolytes with a different pH were studied (H_2SO_4 , Na_2SO_4 and KOH , 1 M). The highest capacitance values were achieved with sulphuric acid (196 F g^{-1} as opposed to 140 and 106 F g^{-1} for Na_2SO_4 and KOH , respectively), probably due to its higher ionic conductivity and the basic nature of the oxygen functionalities found on the surface of the carbon xerogel. Nevertheless, because of the corrosive character of sulphuric acid, Na_2SO_4 would be a more suitable electrolyte.

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1. Introduction

Electrochemical capacitors, also known as supercapacitors, have attracted the interest of the scientific and industrial community due to a series of advantages including their high power density, long durability and maintenance-free operation [1–5]. These unique features make them suitable devices for a wide range of applications as hybrid electric vehicles, telecommunications systems, portable electronic applications or solar/wind power plants, all of which require a rapid storage and release of energy at high power rates [1,2,5]. Electric energy storage in carbon material-based supercapacitors is mainly based on the separation of

charged species by means of the electric double-layer (EDL) formed at the electrode/electrolyte interface (purely electrostatic energy storage). However, charge storage capacity can be enhanced by redox reactions between electrolyte ions and electrode surface functionalities [1,4–7]. Both electric double-layer formation and pseudocapacitance are interfacial phenomena, so electrodes for this type of electrochemical device need to be composed of materials with a high specific surface area ($S_{\text{BET}} > 2000 \text{ m}^2 \text{ g}^{-1}$). Furthermore, when the charge storage is the result of faradaic reactions, electroactive species must be present on the electrode surface (i.e. O, N, B, P, etc.) in combination with aqueous electrolytes [4–7].

Aqueous solutions have several advantages over organic electrolytes since, firstly, they allow oxidation/reduction processes between electrolyte ions and the electrode surface, thereby facilitating extra energy storage and, secondly, they are cheaper,

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environmentally friendly and more conductive [8–11]. However, although aqueous solutions are more favourable, their main limitation is a reduced energy storage capacitance due to their low operating voltage (theoretical stability window of water = 1.23 V). In recent years, several strategies have been proposed to increase the working voltage in aqueous supercapacitors (for example, the use of asymmetric systems based on dissimilar electrode materials [12–16]). Furthermore, as mentioned above, specific capacitance can be increased by means of pseudo-faradaic reactions. These reactions occur between ions from the aqueous solution and functionalities in the electrode material. Thus, the type and pH of the electrolyte and cation/anion size have a considerable impact on the pseudo-faradaic processes. Several studies relating to the use of different aqueous solutions as electrolyte in supercapacitors can be found in the literature [8–11,17]. Zhang et al. [11] prepared carbon based-supercapacitors with aqueous solutions with a different pH and they achieved higher gravimetric capacitance values using a solution of KOH, 6 M (supercapacitor capacitance $\sim 60 \text{ F g}^{-1}$). Andreas and co-workers [17] also evaluated the effect of the electrolyte pH on the charge-storage capacitance of a carbonaceous electrode (highly porous C-cloth) and they obtained a much higher energy storage by using an acidic media (H_2SO_4 1 M), as a result of the pseudocapacitance of the quinone-type surface functionalities. These two examples show that pseudocapacitance is not only directly related to the pH of the electrolyte but also to the surface chemistry of the carbon electrode, since each type of surface functionality is oxidised/reduced under different pH conditions.

It is well known that highly porous carbon electrodes are required for superior performance supercapacitors. Microporosity is especially important since it is in the micropores where charge storage takes place. However, larger pore sizes (mesopores) also favour the process as a faster diffusion of electrolyte ions into the micropores is thereby achieved [1,18,19]. For this reason, one of the most promising carbon materials for charge storage is carbon gel. This carbonaceous material is characterized by: (i) a porous structure tuneable according to the synthesis and processing conditions, (ii) a high surface area and porosity, (iii) a high electrical conductivity and finally, (iv) an excellent cycling behaviour, all properties that make them ideal materials for electrochemical applications [12,20–25]. Another required characteristic of any electrode material for supercapacitors is an acceptable production cost. Until recently, carbon xerogels did not satisfy this requirement since they were obtained from a long, tedious and, therefore, rather expensive procedure. However, this problem was solved in 2009 when Arenillas and co-workers [26] showed that it was possible to design and produce carbon xerogels by means of a faster, easier and cheaper synthesis process based on microwave radiation.

Thus, the objective of the present work is to produce high-performance carbon xerogel-based electrodes and evaluate their energy storage capacitance in different types of aqueous supercapacitors. For this purpose, a resorcinol-formaldehyde carbon xerogel was fabricated by means of microwave-assisted synthesis followed by an activation process (using CO_2 as activating agent) in order to increase the microporosity of the final material and thereby improve its charge storage capacity. The electrochemical behaviour of the carbon xerogel was studied in electrochemical cells of diverse dimensions. The electrodes were produced by using two different preparation methods. Furthermore, in order to investigate the effect of the pH media on the electrochemical performance and, more specifically, on the pseudo-faradaic phenomena of the carbon electrode, three aqueous solutions with different pH were employed as electrolyte (H_2SO_4 , Na_2SO_4 and KOH, 1 M).

2. Experimental

2.1. Preparation of the carbon xerogel

The precursor material used in the activation process was an organic xerogel obtained from the polymerization of resorcinol and formaldehyde. The pH of the resorcinol/formaldehyde mixture was adjusted to a value of 6.5 by adding drops of a sodium hydroxide solution (1 M). Once the precursor solution was prepared, it was subjected to microwave heating in order to induce and accelerate polymerization reactions between the two types of monomers. More details on the microwave-assisted synthesis of organic xerogels can be found in Refs. [27,28]. The organic xerogel (OX) obtained had a specific surface area, S_{BET} , of around $200 \text{ m}^2 \text{ g}^{-1}$ and a helium density of 1.3 g cm^{-3} .

The OX sample was crushed and sieved to between 1 and 2 mm before the physical activation. The device used for the activation process was a vertical tubular reactor, previously purged with nitrogen for approximately 20 min. The activation temperature was 1000°C , the heating rate $50^\circ\text{C min}^{-1}$ and the sample was kept at this maximum temperature for 2 h.

2.2. Physicochemical characterization of the activated carbon xerogel

The textural characteristics of the activated carbon xerogel, ACX, were evaluated from the N_2 adsorption–desorption isotherms recorded at 77 K (*Micromeritics Tristar 3020*). The specific surface area, S_{BET} , was calculated by means of the BET equation and the micropore volume ($V_{\text{DUB-N}_2}$) was determined by applying the Dubinin–Radushkevich (DR) method to the N_2 adsorption isotherm. The pore size distribution was obtained by applying the DFT method and the total pore volume (V_p) was ascertained from the amount of nitrogen adsorbed at saturation point ($p/p^\circ = 0.99$).

The chemical properties of the ACX sample were evaluated by elemental analysis. The C, N and H content was determined on a *LECO-CHNS-932* microanalyzer and the amount of oxygen with a *LECO-TF-900*. The surface chemistry characterization was carried out by temperature-programmed desorption (TPD) measurements and from the point of zero charge (PZC). TPD experiments were performed on a *Micromeritics AutoChem II* analyzer, by heating the samples up to 1000°C in an Argon flow ($50 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate of $10^\circ\text{C min}^{-1}$. The amount of CO , CO_2 and H_2O desorbed was monitored on a mass spectrometer (*OmniStar Pfeiffer*).

2.3. Electrode preparation

To conduct the experiments shown in this study, two types of electrode were prepared: (i) 1 cm^2 disc-shaped electrodes with a thickness of 200–300 μm and, (ii) 4 cm^2 square-shaped electrodes with a thickness of 250–300 μm .

The disc-shaped electrodes were prepared by mixing the activated carbon xerogel (90 wt. %) and polytetrafluoroethylene (PTFE) binder (10 wt. %). The PTFE binder was a solution 60 wt. % in H_2O (Aldrich). Once a homogeneous mixture of both compounds was obtained, the slurry of the mixture was rolled out in order to form a thin film. Electrodes were manufactured by punching pellets (diameter = 1 cm) from the composite based paste. Afterwards, they were pressed and dried before being inserted into the electrochemical cells. The weight of the 1 cm^2 electrodes ranged between 5 and 6 mg.

The larger size electrodes (4 cm^2 , square in shape) used for this study were prepared using a casting procedure. A slurry was obtained from mixing the ACX sample (80 wt. %), graphite fibres (10 wt. %), polyvinylidene fluoride (PVDF) binder (10 wt. %) and the

solvent *N,N*-dimethylacetamide (DMA). In this case, the binder used was a solution 2 wt. % PVDF in DMA. The slurry was then spread over a glass plate by means of a film applicator and left to evaporate at 50 °C for at least 15 h. The composite electrode thus formed was further dried at 70 °C and then thermally treated at 160 °C for 20 min to improve the mechanical strength of the electrodes. The electrodes mass ranged between 20 and 30 mg, but due to their large size, the densities were very similar to those of the previous electrodes ($\sim 6 \pm 1 \text{ mg cm}^{-2}$).

For purposes of identification, the electrodes were denoted as E1 (1 cm^2 pelletized electrodes) and E4 (4 cm^2 electrodes).

2.4. Electrochemical measurements

Electrode material characterization was performed using a two-electrode cell configuration. This configuration was selected because it provides the most accurate measurements of electrode material performance in supercapacitors. Two supercapacitors with different dimensions were assembled in order to evaluate the electrochemical performance of activated carbon xerogel. One of these was a Teflon Swagelok® two-electrode cell filled with stainless steel current collectors, a fibre glass separator ($400 \mu\text{m}$) and two E1 electrodes. The other cell was composed of two 4 cm^2 electrodes (E4) separated by a porous paper of around $60 \mu\text{m}$ thickness (NKK-Japan) and graphite plate current collectors. The electrolytes employed in both of the assembled cells were: H_2SO_4 , Na_2SO_4 and KOH solutions (1 M).

The electrochemical measurements were carried out using a potentiostat/galvanostat Autolab PGSTAT 30 (Eco Chemie, BV, The Netherlands) and the following techniques: (i) cyclic voltammetry at different voltage sweep rates (from 2 to 100 mV s^{-1}) in a voltage window of 1.0 V; (ii) galvanostatic charge/discharge measurements at several current densities (in the range of $0.2\text{--}1.0 \text{ A g}^{-1}$) with $U = 1.0 \text{ V}$ and, (iii) impedance spectroscopy at frequencies ranging between 10 MHz and 1 mHz and with open circuit voltage. The impedance measurements were performed using a potentiostat PGSTAT 30 equipped with a FRA2 module. Due to the different ACX ratios used in each type of electrodes, the specific capacitance values (calculated from the galvanostatic charge/discharge cycles) were expressed in Farads per mass of active material per electrode (F g^{-1}).

3. Results and discussion

3.1. Physicochemical properties of ACX xerogel

The N_2 adsorption–desorption isotherm of the carbon xerogel (Fig. 1a) is a combination of type I and type IV isotherms (micro-mesoporous materials) according to the IUPAC classification [29]. It displays a remarkable hysteresis loop (p/p° ranging from 0.5 to 0.9), which is related to the presence of medium size mesopores, as is evidenced by the pore size distribution (PSD) shown in Fig. 1b. From this PSD, it can be seen that this activated carbon xerogel has a well-developed porosity. On the one hand, there is an ample volume of micropores (i.e. $V_{\text{DUB-N}_2}$ close to $1 \text{ cm}^3 \text{ g}^{-1}$), whose diameter is approximately 1.5 nm, and, on the other hand, there are two different mesopore groups (narrow mesopores with a pore diameter between 2 and 4 nm, and medium size mesopores with a pore diameter that does not exceed 16 nm). All of the information provided by Fig. 1, is corroborated by the pore data collected in Table 1.

Table 1 also contains data concerning the chemical characterization of the ACX sample. As can be seen, the carbon xerogel is mainly composed of C (around 97 wt. %) with a small amount of oxygen (i.e. $O = 2.1 \text{ wt. \%}$). Although the presence of oxygen is only slight, it was necessary to identify the type of oxygen functionalities

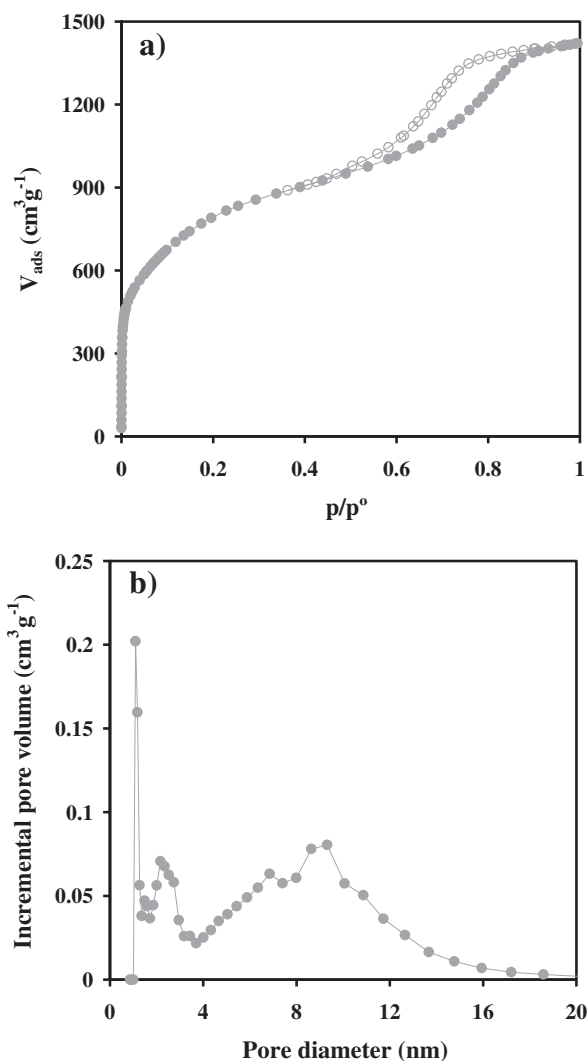


Fig. 1. N_2 adsorption–desorption isotherm (a) and pore size distribution (b) for the activated carbon xerogel used as electrode material.

observed on the carbon xerogel surface. For this purpose, the point of zero charge (pH_{PZC}) was calculated and temperature programmed desorption experiments were carried out. The basic pH_{PZC} (with a value of 8.3) indicates that the oxygen groups have a slightly basic nature, which is corroborated by the TPD results collected in Fig. 2. From the profiles of CO and CO_2 vs. temperature, it can be seen that the presence of oxygen functionalities desorbing as CO_2 (carboxylic acids, anhydrides, lactones [20–32]) is lower and only one peak close to 300°C is observed. The profile of CO presents a maximum peak at around 850°C , which can be attributed to

Table 1
Physico–chemical characteristics of the activated carbon xerogel synthesized.

N_2 adsorption (77 K)			Elemental analysis (wt. % db ^b , ± 0.2)				PZC (± 0.1)
S_{BET} ($\text{m}^2 \text{ g}^{-1}$, ± 10)	$V_{\text{DUB-N}_2}$ ($\text{cm}^3 \text{ g}^{-1}$, ± 0.01)	V_{meso}^a ($\text{cm}^3 \text{ g}^{-1}$, ± 0.01)	C	H	O	N	
2876	0.97	1.28	97.5	0.3	2.1	0.1	8.3

^a $V_{\text{meso}} = V_p - V_{\text{DUB-N}_2}$, where V_p is the volume adsorbed at saturation point ($p/p^\circ = 0.99$).

^b Dry basis.

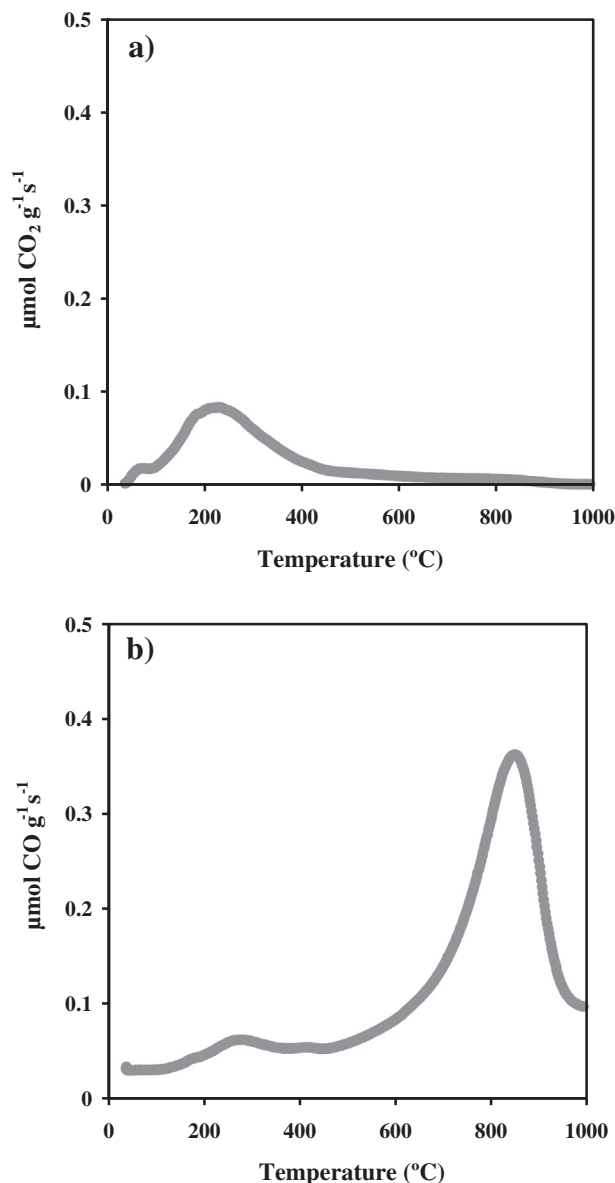


Fig. 2. CO₂ (a) and CO (b) profiles obtained by TPD experiments for the ACX sample.

carbonyl and quinone-like groups, but a small peak that appears at a temperature of approximately 300 °C can also be observed. Both the pH_{PZC} value and the TPD spectra confirm the basic character of the carbon xerogel synthesized in this work. Three aqueous solutions with a different pH were used as electrolyte and therefore, electrode–electrolyte interface of different nature are expected.

3.2. Supercapacitor performance

3.2.1. Electrochemical behaviour of supercapacitors with different dimensions

As mentioned in the [Experimental](#) section, the two types of electrodes were prepared using a specific manufacturing procedure and a particular electrode size (1 and 4 cm²). Furthermore, the cells used in each case for the electrochemical tests were also different (a Swagelok® cell fitted with stainless steel collectors vs. square cell with graphite plate current collectors).

Cyclic voltammograms of the electrochemical cells with H₂SO₄ 1 M as electrolyte and E1 (grey diamonds) and E4 (black circles)

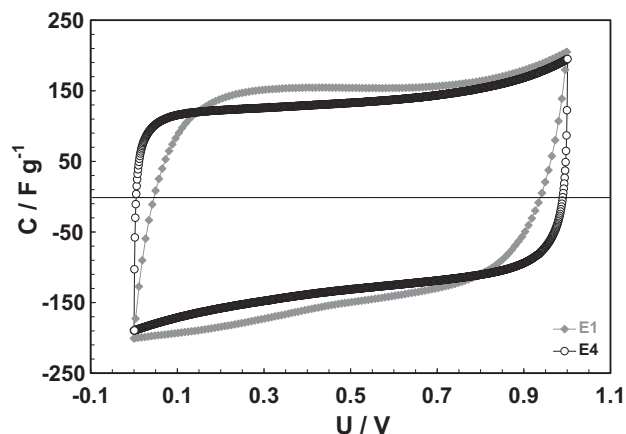


Fig. 3. Cyclic voltammograms for supercapacitors using H₂SO₄ 1.0 M as electrolyte and carbon xerogel-based electrodes of different size (scan rate = 10 mV s⁻¹).

type electrodes are presented in [Fig. 3](#) (voltage range of 1.0 V and scan rate = 10 mV s⁻¹). No significant contribution was observed from the redox reactions involving oxygen functionalities, due to the limited amount of oxygen contained in the carbon xerogel that was used as electrode material ($\text{O} = 2.1 \text{ wt. \%}$). However, although both voltammograms present the typical rectangular behaviour expected for an ideal supercapacitor with quick charge propagation, a slight distortion can be appreciated in the curve obtained with the 1 cm² two-electrode cell (E1), possibly as a result of the contact resistance between the electrodes and current collectors (the ionic resistance of the electrolyte solution, H₂SO₄, is assumed to be the same in both cases) and the method of preparing the electrodes. The addition of carbon fibres and the heat treatment to which the 4 cm² electrodes were subjected, were intended to enhance their mechanical and electrical properties and, according to the results presented in this section, it seems that little improvement was achieved.

[Fig. 4](#) shows the specific capacitance values for the carbon xerogel-based electrode (E1 as opposed to E4) as a function of current density. The data were derived from the galvanostatic charge/discharge profiles obtained using different current loads (from 0.2 to 1.0 A g⁻¹) in a voltage window of 1.0 V. As expected,

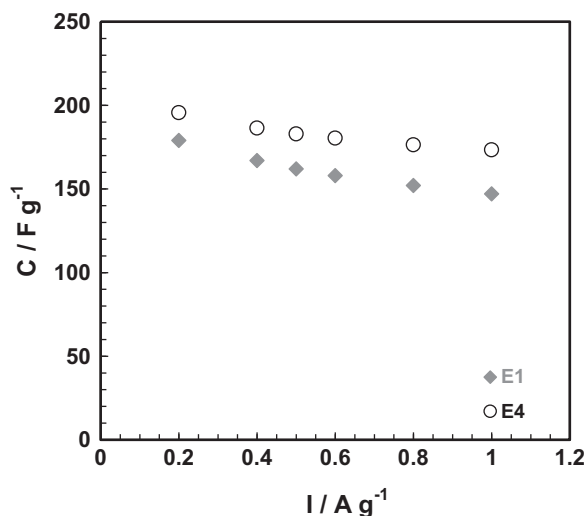


Fig. 4. Variation of specific capacitance (F g^{-1}) with current density for cells built with 1 and 4 cm² electrodes and H₂SO₄ 1 M as electrolyte (maximum voltage = 1.0 V).

energy storage capacitance decreases as the current density increases, from 196 to 173 F g⁻¹ for the type E4 electrodes and from 179 to 147 F g⁻¹ for the 1 cm² electrodes. However, the most interesting feature of these results concerns the high energy storage capacitance achieved with the carbon xerogel (values close to 200 F g⁻¹). Also, worthy of note are the excellent electrochemical performance of the E4 type electrodes (i.e., those with an electrode surface of 4 cm² and better mechanical properties), and the high carbon loadings (~5 mg cm⁻³), which suggests that with electrodes based on carbon xerogels and produced on an industrial scale (optimized manufacturing process), energy storage devices with a high specific capacitance can be obtained.

3.2.2. Influence of the electrolyte pH on the energy storage capacitance of activated carbon xerogel

The carbon xerogel synthesized in this work was tested as supercapacitor electrode material (electrode surface: 4 cm²) in aqueous solutions with a different pH (H₂SO₄, Na₂SO₄ and KOH). It is well known that the nature of the electrolyte influences the charge storage capacity of the electrode material via: (i) the ionic radius of the electrolytes (free and solvated ion electrolyte), (ii) the conductivity of the ions and, (iii) ion mobility [11]. The radii of the solvated anions and cations in bulk solution for the electrolytes used in this study are: 3.58 Å (Na⁺), 3.31 Å (K⁺), 2.80 Å (H⁺), 3.79 Å (SO₄²⁻) and 3.00 Å (OH⁻) [11,33]. In addition to the different ionic radii, which affect the access of the ions to the pores of the electrode material, ionic conductivity is also a crucial factor that affects the performance of the supercapacitor. The molar conductivities of the ions used in this work are: 50.1 cm² Ω⁻¹ mol⁻¹ (Na⁺), 73.5 cm² Ω⁻¹ mol⁻¹ (K⁺), 349.8 cm² Ω⁻¹ mol⁻¹ (H⁺), 79.8 cm² Ω⁻¹ mol⁻¹ (SO₄²⁻) and 198 cm² Ω⁻¹ mol⁻¹ (OH⁻) [11]. These data suggest that a different energy storage capacitance can be expected for each electrolyte and this diverse electrochemical performance may be closely related to the conductivity and mobility of the ions and the surface chemistry of the electrode material.

Fig. 5 compares the cyclic voltammograms of the supercapacitors assembled with ACX xerogel in various aqueous media (voltage range from 0 to 1 V; scan rate = 10 mV s⁻¹). As can be seen, the three solutions produce an almost box-shaped curve, reflecting the quasi-capacitive behaviour of the devices studied. Moreover, the figure evidences the largest specific capacitance obtained in the acidic medium, probably due to its higher ionic conductivity, which is consistent with the literature data [15,17,34]. The Na₂SO₄-based electrolyte produces almost the same electrochemical response as sulphuric acid. However, its higher resistivity, evidenced by a slight

deviation from the box-like behaviour of the voltammogram, leads to a lower charge storage capacitance, as is confirmed by the galvanostatic charge–discharge results reported in Fig. 4.

The working voltage used in the cyclic voltammetry tests ($U = 1.0$ V) prevents water electrolysis (1.23 V) and, therefore, faradaic processes from occurring between the electrode material and electrolyte. One possible way to identify the presence of redox reactions, without appreciable peaks in the voltammograms, is to observe the dependence of energy storage on the scan rate or current density. Therefore, charge–discharge tests from 0 to 1 V were carried out using increasing current densities (from 0.2 to 1.0 A g⁻¹).

The gravimetric capacitance values (Farads per gram of ACX xerogel in one electrode) as a function of current density for the three media tested are listed in Table 2. When a neutral and acidic solution was used as electrolyte, there was a decrease in energy storage capacitance (a C reduction of 11.7 and 11.4% for Na₂SO₄ and H₂SO₄, respectively, when the current load was increased from 0.2 to 1.0 A g⁻¹), suggesting the possible contribution of pseudocapacitance to the charge storage [12,35]. Both electrochemical systems were equally influenced by the current density. However, a higher specific capacitance was achieved with the H₂SO₄ electrolyte (i.e. 183 F g⁻¹ as opposed to 132 F g⁻¹ in the neutral electrolyte when the current density was 0.5 A g⁻¹), probably as a result of its higher conductivity, faster H⁺ mobility in comparison to sodium cation (Na⁺) and the greater activity of the basic oxygenated groups found on the surface of the electrode material in this acidic medium. Pseudocapacitive effects probably do not have the same origin in these two media since, in the case of H₂SO₄, pseudocapacitance is the result of redox reactions involving oxygen surface groups on the electrode material whereas in the case of the sodium sulphate electrolyte, it may also be in mind the contribution of extraction/insertion processes of Na ions contained in the solution [36], although the latter is believed to be minimized in the case of carbon materials.

In the alkaline electrolyte (KOH 1 M), there is virtually no dependency on the current load since the gravimetric capacitance is maintained at ca. 105 F g⁻¹ throughout the range of currents studied. This reflects the strictly capacitive behaviour of the device. In other words, the oxygenated functionalities present on the electrode material surface are inactive in the basic medium. Consequently, the specific capacitance values are lower than those obtained with the other two electrolytes (e.g., 106 F g⁻¹ when the current load was 0.5 A g⁻¹ vs. 183 and 132 F g⁻¹ for the other two solutions used). According to these results, a superior electrochemical performance was achieved with the H₂SO₄ solution due to its greater ionic conductivity, H⁺ mobility and the activity of oxygen groups in the activated carbon xerogel. However, because of special requirements of commercial supercapacitors where a non-corrosive electrolyte is desired, Na₂SO₄ would be preferable to permit further scale-up, even though its slightly lower energy storage capacitance than the H₂SO₄ solution.

The electrochemical impedance spectroscopy (EIS) data were analyzed by means of Nyquist plots, in which imaginary impedance

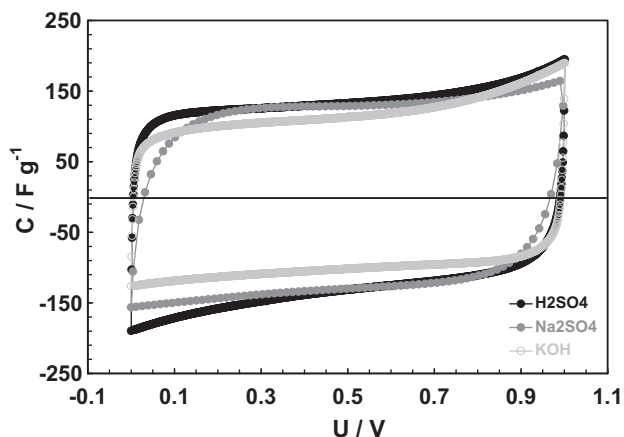


Fig. 5. Cyclic voltammograms obtained in 2-electrode cells (4 cm²) and three electrolytes with a different pH (H₂SO₄, Na₂SO₄ and KOH).

Table 2

Specific capacitance (F g⁻¹) as a function of current density for the ACX electrode in the three aqueous solutions.

Electrolyte	Current density (A g ⁻¹)						C reduction (%)
	0.2	0.4	0.5	0.6	0.8	1.0	
H ₂ SO ₄	196	186	183	180	176	173	11.7
Na ₂ SO ₄	140	135	132	129	127	124	11.4
KOH	106	106	106	105	104	103	2.8

vs. real impedance as a function of frequency is plotted. The Nyquist diagram can also be used to obtain a better insight into the electrochemical behaviour of supercapacitors in different aqueous electrolytes. Because the carbon xerogel has surface oxygen functionalities, these can be expected to show different behaviours depending on the pH of the solution. The Nyquist plot of the AXC cells for the three aqueous electrolytes studied are shown in Fig. 6, with an enlarged view of the high frequency provided in the inset. All the devices display an almost pure capacitive behaviour because of the vertical data point distribution over the entire range of frequencies. A slight deviation (from vertical points) is observed for the supercapacitor equipped with the KOH (1 M) electrolyte. The series resistances (high frequency region) of the devices are equivalent at 0.28, 0.37 and $0.68 \Omega \text{ cm}^{-2}$ for H_2SO_4 , Na_2SO_4 and KOH electrolyte, respectively. These series resistance values are attributed to the ionic resistance of the electrolyte and the contact resistances between the electrode and current collector. The latter was assumed to be constant for all the devices because the same amount of carbon was added in the electrodes and the same current collectors were applied. It is remarkable that, because of the higher ionic conductivity, the supercapacitor with the 1 M H_2SO_4 electrolyte shows the lowest real impedance at all of the frequencies (the Figure is not provided here), but at values close to 1 mHz the resistance of the Na_2SO_4 electrolyte (10.1Ω) approaches that of H_2SO_4 (9.87Ω), which indicates that neutral electrolyte can also be an effective electrolyte for this kind of carbon xerogel. These results are in agreement with recent literature findings on the development of high energy supercapacitors based on neutral aqueous electrolyte (e.g. Na_2SO_4 and Li_2SO_4), which are able to work up to 1.6–2 V [13,16,37–39].

The specific capacitances of the supercapacitors in different aqueous electrolytes were calculated from the impedance analysis employing the imaginary component of impedance. Fig. 7 reports the behaviour of specific capacitance as a function of frequency. The specific capacitance for one electrode is obtained using the equation $C = 4(-1/2\pi f Z'' m)$, where f is frequency in Hz, Z'' is the imaginary component of impedance and m , the mass of xerogel calculated for one electrode. At a frequency of 1 mHz, the values of capacitance for H_2SO_4 , Na_2SO_4 and KOH were 250, 190 and 145 F g^{-1} , respectively, which are higher than the values shown in

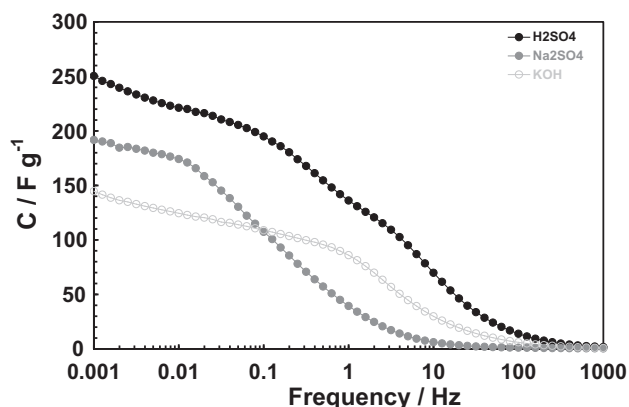


Fig. 7. Gravimetric capacitance (F g^{-1}) as a function of the frequency (Hz) for the supercapacitors assembled with the three aqueous solutions studied.

Table 2, calculated for a current load of 0.2 A g^{-1} using galvanostatic charge and discharge (G-CD) measurements. The differences may be attributed to the different conditions in which the measurements were taken. The impedance was carried out at OCP in alternating current and the G-CD are measurements performed using a continuous current and they are performed at different voltages (from 0 to 1 V). It is thought that by extrapolating the current from G-CD to zero, capacitance could achieve that of impedance at a frequency of 1 mHz. Moreover, it must be borne in mind that the capacitance from impedance analysis is derived from a series-RC circuit model. The capacitances of 250, 190, and 145 F g^{-1} at 1 mHz should be considered as limiting values for these devices in conditions of 0 V. Nevertheless, high values can be obtained with supercapacitors based on electrodes of a large enough size (4 cm^2) and a large enough carbon load ($5 \pm 1 \text{ mg cm}^{-2}$). In short, the electrodes we have developed using an activated carbon xerogel and a casting procedure are fully scalable and almost ready for use in automatized production lines.

All the electrochemical tests performed in this work demonstrate the superior electrochemical performance of an electrochemical cell composed of an ACX sample-sulphuric acid pair. The higher energy storage achieved with this device is basically due to the higher ionic conductivity of H_2SO_4 and the more facile diffusion of the protons (H^+) into the pores of the electrode material. However, the chemical nature of the ACX sample, used as electrode material, is also an important factor to be considered. According to the literature [40,41], the point of zero charge (pH_{PZC}) is the pH at which the total surface charge assumes the value of zero, i.e., when the positive and negative charges compensate each other. Carbon xerogels are characterized by their amphoteric nature [21]; they can be electron donors/acceptors, depending on the pH medium. For this reason, the nature of aqueous electrolyte used in supercapacitors is important since, depending on the type of the electrolyte, the electric charge of the electrode surface can be adjusted in order to permit different energy storage capacitances. When a solution of H_2SO_4 is used as electrolyte (i.e. when the pH_{PZC} of the electrode material is higher than the electrolyte pH) there is a predominance of positive charges in the surface of the carbon material. These may be involved in redox reactions, thereby increasing the capacitance of the electrochemical cell due to pseudo-faradaic phenomena. In a similar way, the use of the basic electrolyte (i.e., KOH) gives rise to a difference between the pH_{PZC} and pH_e but, in this particular case, the surface has an excess of negative charges, which, might be indicative of a different pseudo-faradaic contribution. However, the results obtained from chronoamperometry (complete independence of gravimetric

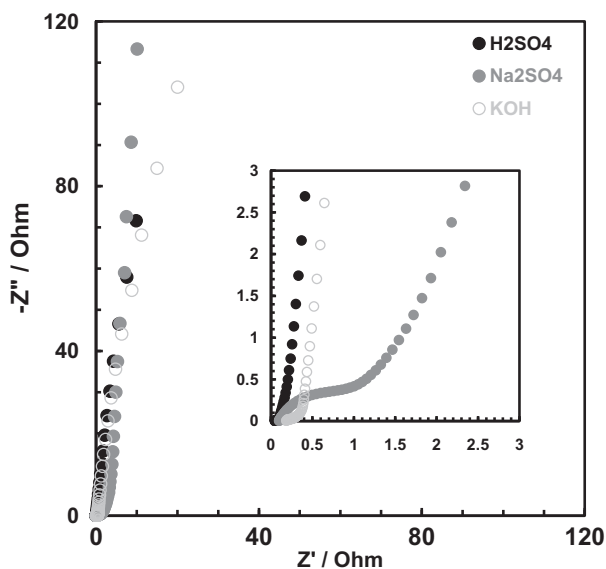


Fig. 6. Nyquist plots for 4 cm^2 two-electrode cells and three different aqueous electrolytes. The inset shows the high frequency region of impedance.

capacitance with current density), suggest that a basic electrolyte promotes charge storage via a purely electrostatic mechanism so, in these operating conditions, it seem that negative charges probably do not play a major role in pseudocapacitive processes.

4. Conclusions

Carbon xerogels can be tailored to have a substantial micropore volume and well-defined mesoporosity. In this study, an activated carbon xerogel with a tailored porosity was used as active material in supercapacitors. The combination of this promising electrode material with three aqueous electrolytes (H_2SO_4 , Na_2SO_4 and KOH , 1 M solutions) and supercapacitors of different dimensions (a Swagelok® cell with 1 cm² electrodes vs. graphite plate collectors using 4 cm² square electrodes) was evaluated in order to optimize the electrochemical behaviour of the supercapacitor.

A supercapacitor built with large carbon xerogel electrodes with superior properties exhibited a higher energy storage capacity than the counterpart device composed of 1 cm² electrodes (196 F g⁻¹ vs. 173 F g⁻¹ for E4 and E1 electrodes, respectively). This finding could be useful for the scaling up of electrodes. If a highly porous carbon xerogel is used for the production of electrodes on an industrial scale, the good behaviour of the device can be ensured.

The influence of the pH of electrolyte on the electrochemical response of supercapacitors based on activated carbon xerogel was also investigated. It was found that the surface chemistry of the active material in combination with the pH of the medium may have a strong influence on pseudocapacitance. It has been shown that the highest gravimetric capacitance is obtained with H_2SO_4 , probably due to its better conductivity and proton mobility and the superior activity of the oxygen functionalities on the carbon xerogel surface. The impedance analysis showed that when $f = 1$ mHz, gravimetric capacitance reached 250 F g⁻¹ with H_2SO_4 as electrolyte, while this value was only 190 and 145 F g⁻¹ for the Na_2SO_4 and KOH electrolytes, respectively, and with the activated carbon xerogel as electrode material. Because of the corrosive nature of acid electrolyte and the high energy storage capacitance demonstrated by Na_2SO_4 , a neutral solution would seem an attractive alternative for aqueous supercapacitors environmentally friendly. The results of this study also show that the combination of an activated carbon xerogel and a basic electrolyte (KOH 1 M) produces a supercapacitor with no pseudocapacitive reactions and, therefore, substantially lower gravimetric capacitance values.

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References

- [1] A.G. Pandolfo, A.F. Hollenkamp, J. Power Sources 157 (2006) 11–27.
- [2] E. Raymundo-Piñero, K. Kierzek, J. Machnikowski, F. Béguin, Carbon 44 (2006) 2498–2507.
- [3] M. Inagaki, H. Konno, O. Tanaiki, J. Power Sources 195 (2010) 7880–7903.
- [4] R. Kötz, M. Carlen, Electrochim. Acta 45 (2000) 2483–2498.
- [5] Y. Zhang, H. Feng, W. Wu, L. Wang, A. Zhang, T. Xia, H. Dong, X. Li, L. Zhang, Int. J. Hydrogen Energy 34 (2009) 4889–4899.
- [6] E. Frackowiak, Phys. Chem. Chem. Phys. 9 (2007) 1774–1785.
- [7] E. Raymundo-Piñero, F. Leroux, F. Béguin, Adv. Mater. 18 (2006) 1877–1882.
- [8] J.H. Chae, G.Z. Chen, Electrochim. Acta 86 (2012) 248–254.
- [9] V. Khomenko, E. Raymundo-Piñero, F. Béguin, J. Power Sources 195 (2010) 4234–4241.
- [10] V. Ruiz, R. Santamaría, M. Granda, C. Blanco, Electrochim. Acta 54 (2009) 4481–4486.
- [11] X. Zhang, X. Wang, L. Jiang, H. Wu, C. Wu, J. Su, J. Power Sources 216 (2012) 290–296.
- [12] F. Lufrano, P. Staiti, E.G. Calvo, E.J. Juárez-Pérez, J.A. Menéndez, A. Arenillas, Int. J. Electrochem. Sci. 6 (2011) 596–612.
- [13] L. Demarcomay, E. Raymundo-Piñero, F. Béguin, Electrochem. Commun. 12 (2010) 1275–1278.
- [14] M.S. Hong, S.H. Lee, S.W. Kim, Electrochem. Solid State Lett. 5 (2002) A227–A230.
- [15] M.P. Bichat, E. Raymundo-Piñero, F. Béguin 48 (2010) 4351–4361.
- [16] X. Zhang, Y. He, G. Jiang, X. Liao, Z. Ma, Electrochem. Commun. 13 (2011) 1166–1169.
- [17] H.A. Andreas, B.E. Conway, Electrochim. Acta 51 (2006) 6510–6520.
- [18] E. Frackowiak, G. Lota, J. Machnikowski, C. Vix-Guterl, F. Béguin, Electrochim. Acta 51 (2006) 2209–2214.
- [19] W. Li, G. Reichenauer, J. Fricke, Carbon 40 (2002) 2955–2959.
- [20] C. Moreno-Castilla, M.B. Dawidziuk, F. Carrasco-Marín, E. Morallón, Carbon 50 (2012) 3324–3332.
- [21] E.G. Calvo, J.A. Menéndez, A. Arenillas, Nanomaterials (2011) 187–234. Mohammed Muzibur Rahman Editorial.
- [22] E.G. Calvo, N. Ferrera-Lorenzo, A. Arenillas, J.A. Menéndez, Microporous Mesoporous Mater. 168 (2013) 206–212.
- [23] G. Rasines, P. Lavela, C. Macías, M. Haro, C.O. Ania, J.L. Tirado, J. Electroanal. Chem. 671 (2012) 92–98.
- [24] K.Y. Kang, S.J. Hong, B.I. Lee, J.S. Lee, Electrochem. Commun. 10 (2008) 1105–1108.
- [25] Y.-M. Chang, C.-Y. Wu, P.-W. Wu, J. Power Sources 223 (2013) 147–154.
- [26] A. Arenillas, J.A. Menéndez, L. Zubizarreta, E.G. Calvo, Patent ES-2000930256, 2009.
- [27] E.G. Calvo, E.J. Juárez-Pérez, J.A. Menéndez, A. Arenillas, J. Colloid Interface Sci. 357 (2011) 541–547.
- [28] E.J. Juárez-Pérez, E.G. Calvo, A. Arenillas, J.A. Menéndez, Carbon 48 (2010) 3293–3311.
- [29] IUPAC Recommendations, Pure Appl. Chem. 57 (1985) 603–619.
- [30] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, S. Shiraishi, Carbon 41 (2003) 4351–4361.
- [31] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J. Órfao, Carbon 37 (1999) 1379–1389.
- [32] N. Mahata, M.F.R. Pereira, F. Suárez-García, A. Martínez-Alonso, J.M.D. Tascón, J.L. Figueiredo, J. Colloid Interface Sci. 324 (2008) 150–155.
- [33] Q.T. Qu, B. Wang, L.C. Yang, Y. Shi, S. Tian, Y.P. Wu, Electrochem. Commun. 10 (2008) 1652–1655.
- [34] C.-C. Hu, C.-C. Wang, J. Power Sources 125 (2004) 299–308.
- [35] A. Malak-Polaczyk, C. Matei-Ghimbeu, C. Vix-Guterl, E. Frackowiak, J. Solid State Chem. 183 (2010) 969–974.
- [36] O.A. Vargas, A. Caballero, L. Hernán, J. Morales, J. Power Sources 196 (2011) 3350–3354.
- [37] K. Fic, G. Lota, M. Meller, E. Frackowiak, Energy Environ. Sci. 5 (2012) 5842–5850.
- [38] P. Staiti, A. Arenillas, F. Lufrano, J.A. Menendez, J. Power Sources 214 (2012) 137–141.
- [39] Q. Gao, L. Demarconnay, E. Raymundo-Piñero, F. Béguin, Energy Environ. Sci. 5 (2012) 9611–9617.
- [40] L.R. Radovic, I.F. Silva, J.I. Ume, J.A. Menéndez, C.A. León y León, A.W. Scaroni, Carbon 35 (1997) 1339–1348.
- [41] P. Burg, D. Cagniant, in: R.L. Radovic (Ed.), Chemistry and Physics of Carbon, 2008, pp. 130–169.